Suspended Spray Reaction for Preparation of Ru/Al_2O_3 Catalyst

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Ru/Al_2O_3 catalysts were prepared by a suspended spray reaction (SSP) method applying a high temperature at 1273 K. The particles of SSP-Ru/Al_2O_3 were spherical sub-micron composites. The ruthenium species were not sintered but highly dispersed with small crystallite size (< 2 nm) over Al_2O_3 that retained the original surface area.

Ru/Al_2O_3 catalysts are highly active for reactions involving hydrogen such as hydrogenolysis of alkanes, hydrogenation of CO, and ammonium synthesis. There is great interest in the preparation of Ru/Al_2O_3 catalysts. As one of the precursors of Ru, $RuCl_3$ is usually used in preparation of Ru/Al_2O_3 catalysts because of easy of handling, low cost, and availability of water-soluble metal salts. Metallic Ru supported catalyst may be synthesized directly by reduction of mixture of $RuCl_3$ and Al_2O_3.[1,2] There, however, have been numerous studies on reduced Ru supported catalysts prepared via ruthenium oxide.[3,4] One of the reasons is that the oxidation at a higher temperature is an effective process to remove the impurities such as residual chlorine. For unsupported ruthenium sample, the chlorine and oxygen strongly bound to the metal atoms in ruthenium oxide, can be considerably diminish by calcinining it in air prior to reduction.[5]

On the other hand the high temperature calcination causes the increase of coalescence of ruthenium oxide and formation of aggregates of larger crystallite. Low dispersion of expensive metal such as ruthenium make the utilization of catalysts more difficult. To solve this problem we have proposed the suspended spray reaction (SSP) method. For SSP method, the mixture of $RuCl_3$ and Al_2O_3 was calcined at high temperatures quickly. We presumed that a very rapid process with quick-heating and quenching is effective to prevent the crystal growth leading active surface. This SSP method is a modification of spray reaction techniques that sometimes called spray pyrolysis or aerosol thermolysis.[6-10] No detailed study using this method for preparing supported metal catalyst has been published.

To prepare Ru/Al_2O_3, Al_2O_3 powder (Al_2O_3-C, Japan Aerosil Co., δ-Al_2O_3, surface area = 100 m^2/g) was suspended in an aqueous solution of $RuCl_3$ ($H_2O : Al_2O_3 = 60 : 1$ /g). The suspension was held at room temperature for 24 h, and then atomized by an ultrasonic device (f = 1.7 MHz) to produce the mist containing Al_2O_3 and $RuCl_3$. The suspension was sprayed without separation of Al_2O_3 and $RuCl_3$. The mist was passed though a quartz tube reactor under the suction of an aspirator where the reactor was externally heated by a furnace controlled at 1273 K. The pyrolysis of $RuCl_3$ proceeded quickly as droplets passed through the high temperature quartz tube in less than a second. The fine particles that were formed were collected by a glass filter. A trap cooled by water was placed between the glass filter and the aspirator to observe residues of the precursor. For comparison, conventional impregnation (IMP) catalysts were prepared by the impregnation of Aerosil Al_2O_3-C with the aqueous solution of $RuCl_3$, subjected to heating in air at 773 K for 2 h. Numerals affixed to name notations, such as SSP-1, SSP-3, IMP-1, and IMP-3, indicate the Ru weight percentage. In the process of preparing ruthenium catalysts, one should note some loss of ruthenium species. Under oxidizing conditions of ruthenium species, volatilization might take place with the formation of RuO_4 (gas) in the vapor phase. The formation of which could not observed during the preparation of both SSP and IMP catalysts. The amount of ruthenium loss during preparation of both methods, therefore,was believed little.

The BET surface area of SSP-1 and SSP-3 indicates that the original support Al_2O_3 remained almost unchanged. The rapid process of quick-heating and quenching may suppress the decrease of the surface area in spite of the high temperature at 1273 K. This agreed with the powder XRD patterns showing no transformation of the support δ-Al_2O_3 through SSP reaction (Figure 1).

The XRD patterns indicated that the crystal peaks of RuO_2 were not detected on either SSP-1 or SSP-3. For both of SSP-1 and SSP-3 treated with hydrogen at 773 K for 1 h, metallic Ru

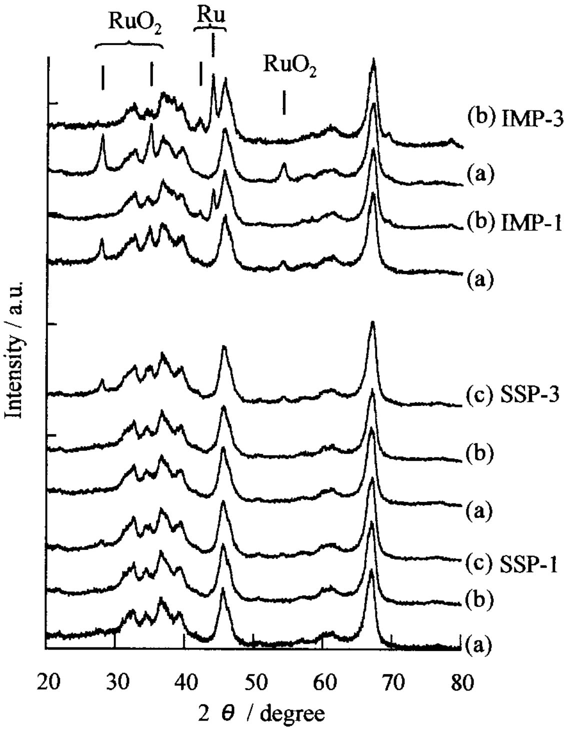

Figure 1. XRD patterns of SSP and IMP-Ru/Al_2O_3
(a) original, (b) after reduction of original,
(c) after oxidation of original.

peaks did not appear and no marked change in the profiles was observed. The XRD patterns suggested that the crystallite sizes of both of the Ru and RuO_2 were small (< 2 nm), or possibly in amorphous states, distributed on the surface of the support. For SSP-1 and SSP-3 subjected to heating in air at 773 K at 2 h, small RuO_2 peaks were observed. Those intensities of RuO_2 peaks were as one third small as those shown in IMP-1 and IMP-3. The rapid process of quick-heating and quenching during preparing Ru/Al_2O_3 seems to be very effective to produce high dispersion of Ru species and to prevent the crystal growth during oxidation after preparation.

The decrease of aggregation of crystallite RuO_2 may be derived from homogeneous distribution and less mobility of the ruthenium oxide. This stability on SSP-1 and SSP-3 suggests strong interaction between ruthenium oxide particles and aluminum oxide.

The temperature programmed reduction profiles show that the reduction temperatures of ruthenium oxide over SSP-1 took place at 477 K, which was approximately 30 K higher than that of IMP-1 (443 K). This difference of the reduction temperatures suggests that ruthenium oxide species were homogeneously distributed as very small particles and possibly part of a ruthenium oxide particle stably buried on the surface of aluminum oxide. This effect was frequently observed for particles prepared from spray reaction method.[9,10] This result agreed with XRD patterns showing of smaller crystal growth of RuO_2.

The CO chemisorption study was carried out on SSP and IMP-Ru/Al_2O_3 treated in hydrogen at 773 K for 1 h. The CO/Ru calculated from CO chemisorption of SSP-1, SSP-3, IMP-1 and IMP-3 were 0.21, 0.25, 0.04 and 0.03, respectively. This revealed that higher dispersions of metallic Ru were obtained for SSP-Ru/Al_2O_3 than those of IMP-Ru/Al_2O_3.

The SEM images showed that the shapes of SSP-Ru/Al_2O_3 particles were sub-micron spheres (d_{ave} = 0.99 μm) that have hollow or shell-like structures (Figure 2). These spherical composites were formed during the calcination of each spherical droplet. This figure also suggests droplets were heated equally from all directions. Most of the catalyst preparation methods such as standard impregnation technique synthesize a wide range of sizes and figures of composites randomly. In this sense the homogeneity of SSP particles has potentials with respect to attain better efficiency and reproducibility to suppress unexpected side reactions in the industrial usage.

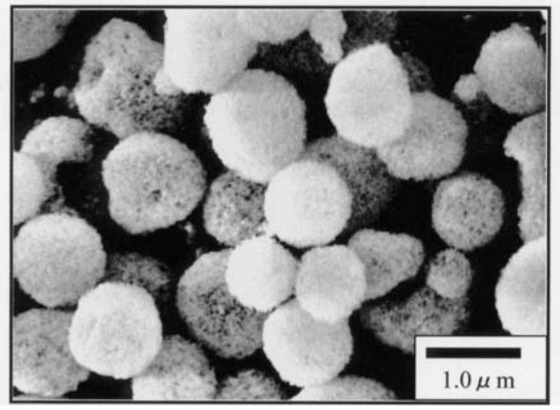

Figure 2. The SEM image of SSP-3.

As a modification of spray techniques SSP method appears to have several advantages and applicability for new catalyst preparation. Further study on the catalytic properties of SSP-Ru/Al_2O_3 will clarify the values of the SSP method.

References and Notes

1 T. Narita, H. Miura, M. Ohira, H. Hondou, K. Sugiyama, T. Matsuda, and R. D. Gonzalez, *Appl. Catal.*, **32**, 185 (1987).

2 M. C. J. Bradford and M. A. Vannice, *J. Catal.*, **183**, 69 (1999).

3 P. Betancourt, A. Rives, R. Hubaut, C. E. Scott, and J. Goldwasser, *Appl. Catal. A.*, **170**, 307 (1998).

4 K. Lu and B. J. Tatarchuk, *J. Catal.*, **106**, 166 (1987).

5 J. A Don, A. P. Pijpers, and J. J. F. Scholten, *J. Catal.*, **80**, 296 (1983).

6 T. T. Kodas, *Angew. Chem., Int. Ed. Engl. Adv. Mater.*, **28**, 794 (1989).

7 S. Che, O. Sakurai, K. Shinozaki, and N. Mizutani, *J. Aerosol Sci*., **29**, 271 (1998).

8 G. L. Messing, S. -C. Zhang, and G.V. Jayanthi, *J. Am. Ceram. Soc*., **76**, 2707 (1993).

9 D. Li, N. Ichikuni, S. Shimazu, and T. Uematsu, *Appl. Catal. A.*, **172**, 351 (1998).

10 D. Li, N. Ichikuni, S. Shimazu, and T. Uematsu, *Appl. Catal. A.*, **180**, 227 (1999).